

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
22 November 2001 (22.11.2001)

PCT

(10) International Publication Number  
**WO 01/87899 A1**

(51) International Patent Classification<sup>7</sup>: **C07F 9/50**,  
9/6568, 9/6571, C07C 45/50, B01J 31/24

(21) International Application Number: PCT/EP01/05625

(22) International Filing Date: 16 May 2001 (16.05.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
00304171.2 17 May 2000 (17.05.2000) EP

(71) Applicant (for all designated States except US): **SHELL  
INTERNATIONALE RESEARCH MAATSCHAPPIJ  
B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 IIR  
The Hague (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **DRENT, Eit**  
[NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).  
**EBERHARD, Michael, Rolf** [DE/GB]; Cantocks Close,  
Bristol, Avon BS8 1TS (GB). **PRINGLE, Paul, Gerard**  
[GB/GB]; Cantocks Close, Bristol, Avon BS8 1TS (GB).

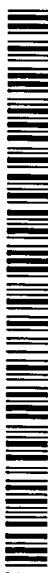
(81) Designated States (*national*): AF, AG, AI, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,  
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,  
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,  
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,  
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 01/87899 A1**

(54) Title: BIDENTATE LIGANDS USEFUL IN CATALYST SYSTEM

(57) Abstract: Bidentate ligand of formula (II)  $R^1R^2M^1-R-M^2R^3R^4$ , wherein  $M^1$  and  $M^2$  are independently P, As or Sb;  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  independently represent tertiary alkyl groups, or  $R^1$  and  $R^2$  together and/or  $R^3$  and  $R^4$  together represent an optionally substituted bivalent cycloaliphatic group whereby the two free valencies are linked to  $M^1$  or  $M^2$ , and R represents a bivalent aliphatic bridging group containing from 2 to 6 atoms in the bridge, which is substituted with two or more substituents. A catalyst system comprising: a) a source of group VIII metal cations, b) a source of such a bidentate ligand, and c) a source of anions. Use of such a catalyst system in a process for the carbonylation of optionally substituted ethylenically or acetylenically unsaturated compounds by reaction with carbon monoxide and a coreactant.

## BIDENTATE LIGANDS USEFUL IN CATALYST SYTEMS

This invention relates to a bidentate ligand of formula I,



wherein  $V^1$  and  $V^2$  are independently P, As or Sb;  $Q^1$ ,  $Q^2$ ,  $Q^3$  and  $Q^4$  represent hydrocarbonyl groups and R represents a bivalent bridging group. The invention further relates to a catalyst system containing such a bidentate ligand, a source of group VIII metal cations and a source of anions. Moreover, the invention relates to a process for the carbonylation of optionally substituted ethylenically or acetylenically unsaturated compounds by reaction with carbon monoxide and a coreactant in the presence of such a catalyst system.

One commercially important carbonylation reaction using hydrogen as coreactant, is the hydroformylation of alkenes or alkynes, which are reacted with carbon monoxide and hydrogen in the presence of transition metal catalysts to form aldehydes and/or alcohols having one carbon atom more than the precursor alkene or alkyne.

Depending on catalyst, reaction conditions and substrates, the hydroformylation may proceed with varying selectivities to the several possible isomeric aldehydes or alcohols in varying yields, as side reactions occur to a smaller or larger extent. Generally only one isomeric product is preferred. For many applications the presence

of branched aldehydes or alcohols is undesirable. Moreover, in view of biological degradability, it is considered advantageous to obtain products having a high content of the linear isomer. The selectivity towards one  
5 of several possible isomeric products is called regioselectivity. For hydroformylation a regioselectivity towards reaction at the primary carbon atom, resulting in a linear product, is desirable.

Another commercially important carbonylation reaction  
10 using an alkanol or water as coreactant, is the carbonylation of alkenes or alkynes, which are reacted with carbon monoxide and alkanol in the presence of Group VIII metal catalysts to form esters, diesters or carboxylic acids. An example of such a carbonylation is  
15 the reaction of ethene with carbon monoxide and butanol to prepare butylpropionates.

CA-A-2086285 relates to the preparation of diphosphines, wherein an alkane, alkene or arene is vicinally disubstituted with two organophosphino groups.  
20 The bidentate diphosphines are said to be useful in the preparation of catalysts for the preparation of polyketones. In example 13 the preparation of 2,3 bis(di-isobutylphosphino)pentane) is described.

WO 9505354 describes the hydroformylation of  
25 ethylenically unsaturated compounds by reaction with carbon monoxide and hydrogen in the presence of a catalyst system comprising a Group VIII metal cation, viz. cationic palladium, and a bidentate ligand, viz. a diphosphine. In the examples several bidentate  
30 diphosphines are used. As is illustrated by examples 46 and 47 the hydroformylation of 1-octene with a catalyst system containing a bidentate diphosphine results in acceptable selectivities towards the linear product. The

results show that the use of a bidentate diphosphine having an unsubstituted bivalent organic bridging group, connecting both phosphorus atoms, i.e.

1,2-bis-(1,4-cyclooctylenephosphino) ethane, results in  
5 higher selectivities towards the linear product than the use of a bidentate diphosphine having an monosubstituted bivalent organic bridging group, connecting both phosphorus atoms, i.e. 1,2-bis(1,4-cyclooctylene-phosphino) propane. Hence, this patent document teaches  
10 that non-substituted bridging groups are advantageous compared to substituted bridging groups.

Although good results with regard to this regio-selectivity towards the linear product are obtained in WO 9505354, there is still room for improvement. This  
15 need especially exists with regard to smaller ethylenically unsaturated compounds, where side-reactions more readily occur.

Examples 28 to 36 of EP-A-0495547 describe a carbonylation of ethene with carbon monoxide and  
20 n-butanol in the presence of bidentate diphosphines having an unsubstituted bivalent organic bridging group, connecting both phosphorus atoms, i.e. 1,3-bis(di-isopropylphosphino) propane; 1,3-bis(di-ethylphosphino) propane; 1,3-bis(di-s-butylphosphino) propane, 1,3-bis-  
25 (di-phenylphosphino) propane. Selectivities of 98% and rates of conversion in the range from 100 to 1000 mol butylpropionate/mol Pd/hr are obtained.

Although good results with regard to selectivity and activity are obtained in EP-A-0495547, there is still  
30 room for improvement.

It has now surprisingly been found that when carbonylation is carried out in the presence of a catalyst system that is characterized by a specific

choice of bidentate ligand containing a polysubstituted bridging group, unexpected advantages with regard to the regioselectivity and/or activity are obtained.

Accordingly this invention provides a bidentate  
5 ligand of formula II,



wherein  $M^1$  and  $M^2$  are independently P, As or Sb;  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  independently represent tertiary alkyl groups, or  $R^1$  and  $R^2$  together and/or  $R^3$  and  $R^4$  together represent  
10 an optionally substituted bivalent cycloaliphatic group whereby the two free valencies are linked to  $M^1$  or  $M^2$ , and R represents a bivalent aliphatic bridging group containing from 2 to 6 atoms in the bridge, which is substituted with two or more substituents.

15 Surprisingly it was found that a catalyst system comprising such a bidentate ligand having a polysubstituted bivalent aliphatic bridging group results in a high regioselectivity towards the linear product and/or a higher activity.

20 In the bidentate ligand of formula II,  $M^1$  and  $M^2$  are preferably the same and more preferably they both represent phosphorus atoms.

By "a bridge" is understood the shortest connection between the atoms  $M^1$  and  $M^2$ . This bridge can be saturated  
25 or non-saturated or can form part of an optionally substituted saturated or non-saturated aliphatic ring structure, comprising one or more rings. The bridge can further contain heteroatoms such as nitrogen, sulphur, silicon or oxygen atoms. Preferably at least the atoms in  
30 the bridge connected to  $M^1$  and  $M^2$  are carbon atoms, more preferably all atoms in the bridge are carbon atoms.

The bridge connecting  $M^1$  and  $M^2$  forms part of a bridging group R, which can be saturated or unsaturated and which can be an optionally substituted saturated or non-saturated aliphatic ring structure, such as for  
5 example cyclohexane, cyclohexene, cyclopentane or cyclopentene. The bridging group can further contain heteroatoms such as nitrogen, sulphur, silicon or oxygen atoms. Unsaturated bonds and/or heteroatoms can be present in each part of the bridging group R, both within  
10 and outside the bridge. If the bridging group R is a cycloaliphatic ring structure, the ring may be interrupted by one or more heteroatoms such as nitrogen, sulphur, silicon or oxygen atoms. The aliphatic ring structure can further be substituted with any kind of  
15 substituent, including heteroatoms, alkylgroups, cycloalkyl groups and aryl groups, both within as well as outside the bridge.

The bivalent aliphatic bridging group R, connecting the atoms  $M^1$  and  $M^2$  contains from 2 to 6 atoms in the  
20 bridge, more preferably 2 to 4 atoms, and most preferably 2 to 3 atoms. Preferably the atoms in the bridge are carbon atoms. Bivalent aliphatic bridging groups R, containing 2 carbon atoms in the bridge are especially preferred.

25 The bridge is substituted with at least two substituents. Preferably the bridge is substituted with two to four substituents and more preferably with two to three substituents. Most preferably the bridge is substituted with two substituents. The substituents can  
30 be substituted to any part of the bridge, but are preferably substituted on carbon atoms of the bridging group connected to  $M^1$  and  $M^2$ . A preferred bridging group

is thus a bridging group R having from 2 to 6 carbon atoms in the bridge, wherein the carbon atoms of the bridging group connected to  $M^1$  and  $M^2$  are both substituted with at least one substituent. The carbon atoms of the bridging group connected to  $M^1$  and  $M^2$  are preferably substituted with only one substituent, but they can be substituted with two substituents.

In addition to the carbon atoms connected to  $M^1$  and  $M^2$ , the bridging group can be substituted at other parts, with any kind of substituent, including heteroatoms, alkylgroups, cycloalkyl groups and aryl groups.

In case the substituents are substituted at carbon atoms of the bridge connected to the atoms  $M^1$  and  $M^2$ , the bidentate ligand has chiral C-atoms and can have a R,R, S,S or R,S meso form or mixtures thereof. Both the meso form as well as racemic mixtures can be used.

The substituents on the bridge can be independent or connected. If the substituents are connected, the whole of the substituents and the bridge together can form a bridging group that is an aliphatic ring structure as described herein before. The substituents can further contain carbon atoms and/or hetero atoms.

Suitable substituents include groups containing hetero-atoms such as halides, sulphur, phosphorus, oxygen and nitrogen. Examples of such groups include chloride, bromide, iodide, thiol, and groups of the general formula  $H-O-$ ,  $X^1-O-$ ,  $-S-X^1$ ,  $-CO-X^1$ ,  $-NH_2$ ,  $-NHX^1$ ,  $-NX^1X^2$ ,  $-CO-NX^1X^2$ ,  $-OH$ ,  $-PO_4$ ,  $-NO_2$ ,  $-NOH$ ,  $-CO$ ,  $-SO_2$ ,  $-SOH$ , in which  $X^1$  and  $X^2$ , independently, represent aliphatic groups, preferably having from 1 to 10 carbon atoms, more

preferably having from 1 to 4 carbon atoms, like methyl, ethyl, propyl and isopropyl.

Preferably the substituents are hydrocarbyl groups. The hydrocarbyl groups itself can be aromatic, aliphatic or cycloaliphatic. The hydrocarbyl groups can contain carbon atoms and hetero atoms. Suitable hydrocarbyl groups can further include groups containing hetero-atoms such as the ones mentioned hereinabove. The hydrocarbyl groups include straight-chain or branched saturated or non-saturated carbon containing groups.

Suitable aromatic hydrocarbyl groups include aryl groups such as phenyl groups or naphthyl groups, and alkyl phenyl groups such as tolyl groups. Of these, substitution with phenyl groups is preferred.

Preferably the hydrocarbyl groups are alkyl groups, preferably having from 1 to 10 carbon atoms, more preferably from 1 to 4 carbon atoms. Linear, branched or cyclic alkyl groups can be used. Suitable alkyl groups include, methyl, ethyl, propyl, iso-propyl, butyl and iso-butyl. More suitably methyl groups are used.

Most preferably the bridge is di-substituted, preferably with two alkyl groups, most preferably with two methyl groups. In an advantageous embodiment the substitution is vicinal.

Examples of bivalent aliphatic bridging groups that can be used include cyclopentane, cyclopentene, cyclohexane, cyclohexene, butane, 1-butene, 2-butene, pentane, 2-pentene, diphenylethane, diethylether, 1,2-diphenylpropane, 2,3-diphenylbutane.

$R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  can independently represent a tertiary alkyl group. By a tertiary alkyl group is understood an alkyl group which is connected to the phosphorus atom by a tertiary carbon atom. The tertiary



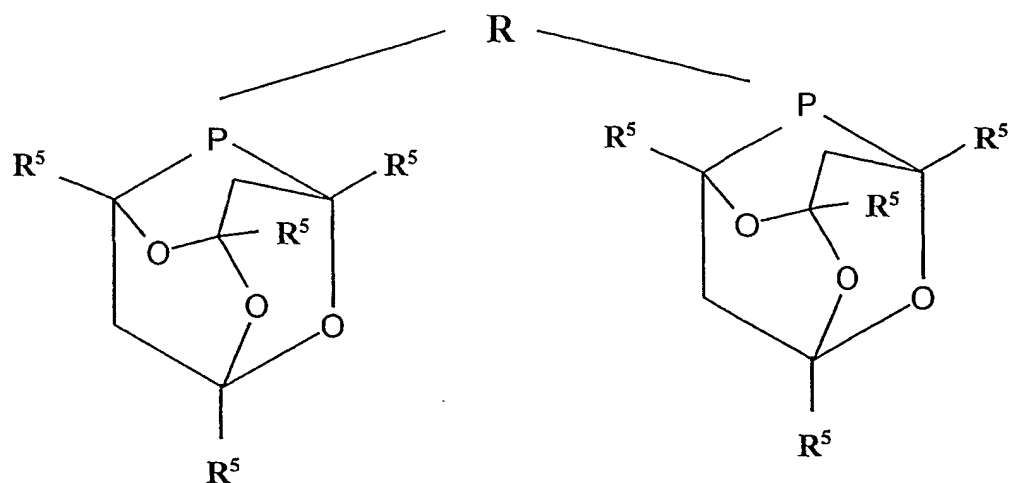
alkyl group preferably has from 4 to 20 carbon atoms, more preferably from 4 to 8 carbon atoms. Examples of suitable non-cyclic tertiary alkyl groups are tertiary butyl, 2-(2-methyl)butyl, 2-(2-ethyl)butyl, 5 2-(2-methyl)pentyl and 2-(2-ethyl)pentyl groups. Preferably the groups  $R^1$  to  $R^4$  represent the same tertiary alkyl groups, most preferably  $R^1$  to  $R^4$  are tert-butyl groups.

Examples of possible ligands include 2,3-bis(di- 10 tertiarybutylphosphino)butane, 2,3-bis(di-tertiary-butylphosphino)butene, 2,4-bis(di-tertiarybutylphosphino)pentane, 2,4-bis(di-tertiarybutylphosphino)pentene, 1,2-bis(di-tertiarybutylphosphino)cyclopentane, 1,2-bis(di-tertiarybutylphosphino)pent-1-ene, 2,3-bis(di- 15 tertiary-butylphosphino)pentane, 2,4-bis(di-tertiary-butylphosphino)hexane, 3,4-bis(di-tertiary-butylphosphino)hexane, 2,3-bis[di-2-(2-methyl)butylphosphino]butane, 2,3-bis[di-2-(2-ethyl)butylphosphino]butane. A very suitable bidentate diphosphine 20 is 2,4-bis(di-tertiarybutylphosphino)pentane.

$R^1$  and  $R^2$  together and/or  $R^3$  and  $R^4$  together can also represent an optionally substituted bivalent cycloaliphatic group.

A special class of bivalent cycloaliphatic groups 25 include tertiary cyclic structures. For example  $R^1$  and  $R^2$  and/or  $R^3$  and  $R^4$  can represent a bivalent radical that together with the phosphorus atom to which it is attached is an alkyl substituted 2-phosphatricyclo[3.3.1.1{3,7}]-decyl group or a derivative thereof in which one or more 30 of the carbon atoms are replaced by heteroatoms. Preferably the ligand comprising the alkyl substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group is a compound

according to Formula III, wherein  $R^5$  are alkyl groups of 1-6 carbon atoms, preferably methyl.



5           Examples of possible ligands include 2,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-[3.3.1.1{3.7}decyl)butane and 2,4-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}-  
10           decyl)pentane. Such ligands can be prepared as described in more detail in WO-A-9842717.

          In an especially preferred embodiment  $R^1$  and  $R^2$  together and/or  $R^3$  and  $R^4$  together represent an optionally substituted bivalent cycloaliphatic group. More preferably both  $R^1$  and  $R^2$  together and  $R^3$  and  $R^4$   
15           together represent such an optionally substituted bivalent cycloaliphatic group. This optionally substituted bivalent cycloaliphatic group preferably comprises at least 5 ring atoms and more preferably contains from 6 to 10 ring atoms. It is advantageous that  
20           the cycloaliphatic group is a cycloalkylene group, i.e. forming with the atom  $M^1$  or  $M^2$  a bicyclic group. Preferably  $M^1$  and  $M^2$  are both phosphorus and  $R^1$ ,  $R^2$  and  $M^1$  together and  $R^3$ ,  $R^4$  and  $M^2$  together both represent a

phosphabicyclocalkyl group. In a highly preferred embodiment the cyclic group contains 8 ring atoms and forms a 9-phosphabicyclononyl group together with a phosphorus atom. The 9-phosphabicyclononyl group can have several isomeric structures. For the purpose of the invention the [3,3,1] and [4,2,1] isomers are preferred. R<sup>1</sup> and R<sup>2</sup> together and R<sup>3</sup> and R<sup>4</sup> together can have both the same or each a different isomeric structure. Preferably both R<sup>1</sup> and R<sup>2</sup> together and R<sup>3</sup> and R<sup>4</sup> together have the [3,3,1] structure. Compositions of bidentate diphosphines having a high amount of bidentate diphosphine ligand having the [3,3,1] structure for both phosphabicyclononyl groups can be prepared as described in non-pre-published European patent application No. 01300866.9.

Substituents of the bivalent cycloaliphatic group formed by R<sup>1</sup> together with R<sup>2</sup> or R<sup>3</sup> together with R<sup>4</sup>, if any, can be alkyl groups having from 1 to 4 carbon atoms. As a rule, all ring atoms are carbon atoms, but bivalent cyclic groups containing one or more heteroatoms in the ring, such as for example oxygen or nitrogen, atoms are not precluded. Examples of suitable bivalent cyclic groups are 1,4-cyclohexylene, 1,4-cycloheptylene, 1,3-cycloheptylene, 1,2-cyclooctylene, 1,3-cyclooctylene, 1,4-cyclooctylene, 1,5-cyclooctylene, 2-methyl-1,5-cyclooctylene, 2,6-dimethyl-1,4-cyclooctylene and 2,6-dimethyl-1,5-cyclooctylene groups. Preferred bivalent cyclic groups are selected from 1,4-cyclo-octylene, 1,5-cyclo-octylene, and methyl (di)substituted derivatives thereof.

Examples of preferred bidentate ligands include 2,3-PP'bis(9-phosphabicyclo[3,3,1]nonyl)-butane,

2,3-PP'bis(9-phosphabicyclo[4,2,1]nonyl)-butane,  
2,3-PP'bis(9-phosphabicyclo[3,3,1]nonyl)-but-2-ene,  
2,3-PP'bis(9-phosphabicyclo[4,2,1]nonyl)-but-2-ene,  
2,3-PP'bis(9-phosphabicyclo[3,3,1]nonyl)-pentane,  
5 2,4-PP'bis(9-phosphabicyclo[3,3,1]nonyl)-pentane,  
2,3-PP'bis(9-phosphabicyclo[4,2,1]nonyl)-pentane,  
2,4-PP'bis(9-phosphabicyclo[4,2,1]nonyl)-pentane,  
2,3-PP'bis(9-phosphabicyclo[3,3,1]nonyl)-pent-2-ene,  
2,3-PP'bis(9-phosphabicyclo[4,2,1]nonyl)-pent-2-ene,  
10 1,2-PP'bis(9-phosphabicyclo[3,3,1]nonyl)-cyclopentane,  
1,2-PP'bis(9-phosphabicyclo[4,2,1]nonyl)-cyclopentane,  
1,2-PP'bis(9-phosphabicyclo[3,3,1]nonyl)-cyclohexane,  
1,2-PP'bis(9-phosphabicyclo[4,2,1]nonyl)-cyclohexane and  
mixtures thereof.

15        These ligands can be prepared by reacting P-cyclo-  
octylene hydride (phosphabicyclononane hydride) and  
butyllithium to generate a lithium cyclo-octylene  
phosphide (lithiated phosphabicyclononane). The later  
phosphide is reacted with an aliphatic group substituted  
20 with suitable leaving groups, preferably tosylates or  
cyclic sulfates, in an appropriate manner. Preferred  
aliphatic groups are those having a cyclic sulfate  
structure as a leaving group, such as cyclic substituted  
or non-substituted alkane diol sulfate esters, also  
25 called cyclic alkyl sulfates. For example 2,4-PP'bis(9-  
phosphabicyclo[3,3,1]nonyl)-pentane can be prepared by  
reacting phosphabicyclononane hydride and butyllithium to  
generate the corresponding lithium phosphide and  
subsequently reacting this lithium phosphide, at for  
30 example 0 °C or ambient temperature (25 °C) in  
tetrahydrofuran, with 2,4 pentanediol di-p-tosylate  
ester. 2,3-PP'bis(9-phosphabicyclo[3,3,1]nonyl)-butane  
can for example be prepared by reacting

phosphabicyclononane hydride and butyllithium to generate the corresponding lithium phosphide and subsequently reacting this lithium phosphide with 2,3-butanediol cyclic sulfate ester (IUPAC name cyclic 2,3-butyl sulfate), in for example tetrahydrofuran at a temperature varying in the range from 0 °C to reflux temperature.

The P-cyclo-octylene hydride (phoshabicyclononane hydride) may conveniently be prepared as described by Elsner et al. (Chem. Abstr. 1978, vol. 89, 180154x).

The invention further provides a catalyst system including:

- (a) a source of group VIII metal cations;
- (b) a bidentate ligand as described above; and
- (c) a source of anions.

In the present specification the group VIII metals are defined as the metals rhodium, nickel, palladium and platinum. Of these, palladium and platinum are preferred.

Examples of suitable metal sources are platinum or palladium compounds such as salts of palladium or platinum and nitric acid, sulphuric acid or sulphonic acids, salts of platinum or palladium and carboxylic acids with up to 12 carbon atoms, palladium- or platinum complexes, e.g. with carbon monoxide or acetylacetonate, or palladium or platinum combined with a solid material such as an ion exchanger. Palladium(II) acetate and platinum(II) acetylacetonate are examples of preferred metal sources.

As anion source, any compound generating these anions may be used. Suitably, acids, or salts thereof, are used as source of anions, for example any of the acids mentioned above, which may also participate in the salts of the metals of the platinum group.

In the catalyst systems of the invention, preferably acids are used as anion source having a pKa value of less than 6, more preferably less than 5, measured in aqueous solution at 18 °C.

5        Typical examples of suitable anions are anions of carboxylic acids, phosphoric acid, sulphuric acid, sulphonic acids and halogenated carboxylic acids such as trifluoroacetic acid.

10        Carboxylic acids that can be used include carboxylic acids with up to 12 carbon atoms, such as for example, pentanoic acid, pivalic acid, propionic acid and propenoic acid.

15        Sulphonic acids are in particular preferred, for example methanesulphonic acid, trifluoromethanesulphonic acid, tert-butane-sulphonic acid, p-toluenesulphonic acid and 2,4,6-trimethylbenzene-sulphonic acid.

20        Also, complex anions are suitable, such as the anions generated by a combination of a Lewis acid such as  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{SnF}_2$ ,  $\text{Sn}(\text{CF}_3\text{SO}_3)_2$ ,  $\text{SnCl}_2$  or  $\text{GeCl}_2$ , with a protic acid, such as a sulphonic acid, e.g.  $\text{CF}_3\text{SO}_3\text{H}$  or  $\text{CH}_3\text{SO}_3\text{H}$  or a hydrohalogenic acid such as  $\text{HF}$  or  $\text{HCl}$ , or a combination of a Lewis acid with an alcohol. Examples of such complex anions are  $\text{BF}_4^-$ ,  $\text{SnCl}_3^-$ ,  $[\text{SnCl}_2.\text{CF}_3\text{SO}_3]^-$  and  $\text{PF}_6^-$ .

25        The invention further provides a process for the carbonylation of optionally substituted ethylenically or acetylenically unsaturated compounds by reaction with carbon monoxide and a coreactant in the presence of a catalyst system as described above.

30        The ethylenically or acetylenically unsaturated compound, used as starting material, is preferably an ethylenically or acetylenically unsaturated compound

having from 2 to 20 carbon atoms per molecule, or a mixture thereof. They may comprise one or more unsaturated bonds per molecule. Preferred are compounds having from 2 to 6 carbon atoms, or mixtures thereof. The  
5 ethylenically or acetylenically unsaturated compound can further comprise functional groups or heteroatoms, such as nitrogen, sulphur or oxide. Examples include unsaturated carboxylic acids, esters of such acids or alkene nitriles.

10 In a preferred embodiment the ethylenically or acetylenically unsaturated compound is an olefin or mixture of olefins. In a preferred process of the invention, such olefins can be converted by reaction with carbon monoxide and a coreactant with a high  
15 regioselectivity towards the linear product. Suitable ethylenically or acetylenically unsaturated compounds include for example acetylene, ethene, propene, butene, isobutene, pentene, pentene nitriles and methyl 3-pentenoates.

20 In the process of the invention, the unsaturated starting material and the formed product may act as reaction diluent. Hence, the use of a separate solvent is not necessary. Conveniently, however, the carbonylation reaction may be carried out in the additional presence of  
25 a solvent. As such, saturated hydrocarbons, e.g. paraffins and isoalkanes are recommended and furthermore alcohols, the saturated hydrocarbons and alcohols preferably having from 4 to 10 carbon atoms per molecule, such as butanol, ethylhexanol-1, nonanol-1, or in general  
30 terms the alcohols formed as carbonylation product; ethers such as 2,5,8-trioxanonane (diglyme), diethylether and anisole, and ketones, such as methylbutylketone. Solvents, comprising or substantially consisting of

5 sulphones are also preferred. Sulphones are in particular preferred, for example dialkylsulphones such as dimethylsulphone and diethylsulphone and cyclic sulphones, such as sulfolane (tetrahydrothiophene-2,2-dioxide),  
sulfolane, 2-methylsulfolane and 2-methyl-4-ethylsulfolane.

10 The quantity in which the catalyst system is used, is not critical and may vary within wide limits. Usually amounts in the range of  $10^{-8}$  to  $10^{-1}$ , preferably in the range of  $10^{-7}$  to  $10^{-2}$  mole atom of Group VIII metal per mole of ethylenically unsaturated compound are used. The amounts of the participants in the catalyst system are conveniently selected such that per mole atom of platinum group metal from 0.5 to 10, preferably from 1 to 6 moles  
15 of bidentate ligand are used, from 0.5 to 15, preferably from 1 to 8 moles of anion source or a complex anion source.

Furthermore the presence of a small amount of catalyst promoter comprising a source of halide anions,  
20 such as for example HI or HCl, can have a significant favourable effect in that the conversion reaction proceeds at high rate, even at moderate temperatures.

For hydroformylation the coreactant can be molecular hydrogen, or more generally a hydride source. The carbon  
25 monoxide and hydrogen may be supplied in equimolar or non-equimolar ratios, e.g. in a ratio within the range of 5:1 to 1:5, preferably 3:1 to 1:3. Preferably they are supplied in a ratio within the range of 2:1 to 1:2.

The carbonylation can be suitably carried out at  
30 moderate reaction conditions. Hence temperatures in the range of 50 to 200 °C are recommended, preferred temperatures being in the range of 70 to 160 °C. Reaction



pressures in the range of 5 to 100 bar are preferred, lower or higher pressures may be selected, but are not considered particularly advantageous. Moreover, higher pressures require special equipment provisions.

5           The claimed catalyst system can also be useful in conversion reactions other than hydroformylation. In general the coreactant can be represented by NuH, wherein Nu represents the remnant nucleophilic moiety of the coreactant after removal of a hydrogen atom. The nature  
10           of the coreactant largely determines the type of product formed. Preferably the coreactant is a nucleophilic compound having a mobile hydrogen atom, such as an alcohol, an acid, an amine or water. For an alcohol XOH (X being the carbon containing part), the XO moiety is  
15           represented by Nu and accordingly the product is an ester.

          Similarly, the use of an acid XCOOH (Nu = XCOO) will introduce an anhydride group in the product of the mono-carbonylation reaction; the use of ammonia (Nu = NH<sub>2</sub>) or  
20           an amine XNH<sub>2</sub> (Nu = XNH) or X<sub>2</sub>NH (Nu = X<sub>2</sub>N) will introduce an amide group; the use of a thiol XSH (Nu = XS) will introduce a thioester group; and the use of water (Nu = OH) will introduce a carboxy group.

          Preferred coreactants are water, alkanol and  
25           hydrogen.

          Preferred alkanols are alkanols with 1 to 20, more preferably with 1 to 6 carbon atoms per molecule and alkanediols with 2-20, more preferably 2 to 6 carbon  
30           atoms per molecule. The alkanols can be aliphatic, cycloaliphatic or aromatic. Suitable alkanols in the process of the invention include methanol, ethanol, ethanediol, n-propanol, 1,3-propanediol, iso-propanol,

butanol, iso-butanol, tert.butanol, pentanol, hexanol, cyclohexanol and phenol.

The invention will be illustrated by the following non-limiting examples.

5     Example 1

Example 1 was carried out in a 250 ml magnetically stirred autoclave. The autoclave was charged with 10 ml of propene, 40 ml anisole and 10 ml sulfolane, 0.25 mmol of platinum(II) acetylacetonate, 0.3 mmol of meso (R,S) 2,3-bis[(cyclo-octylene)phosphino]butane, 0.3 mmol SnCl<sub>2</sub> and 0.3 mmol HCl. After being flushed, the autoclave was pressurized with carbon monoxide and hydrogen to a partial pressure of 30 bar of each. Subsequently, the reactor was sealed and the contents were heated to 100 °C and maintained at that temperature until the reaction was substantially complete. Complete propene conversion occurred in 0.5 hr, the initial rate of carbonylation was 1000 mol CO/grams atom platinum/hour. The initial rate of carbonylation was defined as the mean rate of carbon monoxide consumption over the first 30% propene conversion. After cooling, a sample was taken from the contents of the reactor and analysed by Gas Liquid Chromatography. The selectivity towards the linear product n-butyraldehyde was 99.0%.

25     Comparative example A

Example 1 was repeated, except that instead of 0.3 mmol meso 2,3 bis[(cyclo-octylene)phosphino] butane, 0.3 mmol ligand 1,2 bis[(cyclo-octylene)phosphino] ethane was used as ligand. A similar rate of reaction was observed. After analysis by Gas Liquid Chromatography it was found that the selectivity towards the linear product n-butyraldehyde was 95.5%.

WO 01/87899

Example 2

Example 2 was carried out in a 250 ml magnetically stirred autoclave. The autoclave was charged with 50 ml of butanol, 0.25 mmol of palladium(II) acetate, 0.33 mmol of meso (R,S) 2,3-PP'bis(phosphabicyclo[3.3.1]nonyl)-butane, 0.75 ml propionic acid, and 0.025 mmol HI. After being flushed, the autoclave was pressurized with carbon monoxide to a partial pressure of 15 bar and ethene to a partial pressure of 10 bar. Subsequently, the reactor was sealed and the contents were heated to 115 °C and maintained at that temperature during 1 hour. The initial rate of carbonylation was 1490 mol CO/grams atom palladium/hour. The initial rate of carbonylation was defined as the mean rate of carbon monoxide consumption over the first 30% ethene conversion. After cooling, a sample was taken from the contents of the reactor and analysed by Gas Liquid Chromatography. Conversion was essentially 100%. The selectivity towards butylpropionate was 99%.

Comparative example B

Example 2 was repeated, except that instead of 0.33 mmol of meso (R,S) 2,3-PP'bis(phosphabicyclo[3.3.1]nonyl)butane, 0.4 mmol 1,2-PP'bis(9-phosphabicyclononyl)ethane) was used as ligand. The initial rate of carbonylation was 840 mol CO/grams atom palladium/hour. Conversion was essentially 100%. A similar selectivity towards butylpropionate was observed.

Example 3

Example 3 was carried out in a 250 ml magnetically stirred autoclave. The autoclave was charged with 30 ml of butanol-1, 0.25 mmol of platinum(II) acetylacetonate, 0.3 mmol of meso (R,S) 2,3-PP'bis(phosphabicyclo[3.3.1]nonyl)butane, 30 ml diglyme, 0.3 mmol phosphoric acid.

After being flushed, the autoclave was pressurized with carbon monoxide to a partial pressure of 30 bar and acetylene to a partial pressure of 1.5 bar. Subsequently, the reactor was sealed and the contents were heated to 125 °C and maintained at that temperature during 5 hour. The initial rate of carbonylation was 2500 mol CO/grams atom platinum/hour. Conversion was essentially 100%. The selectivity towards butylacrylate was 98%.

Comparative example C

Example 2 was repeated, except that instead of 0.33 mmol of meso (R,S) 2,3-PP'bis(phosphabicyclo[3.3.1]nonyl)butane, 0.4 mmol 1,2-PP'bis(9-phosphabicyclononyl)ethane) was used as ligand. The initial rate of carbonylation was 1270 mol CO/grams atom platinum/hour. Conversion was 80%. The selectivity towards butylacrylate was 98%.

C L A I M S

1. Bidentate ligand of formula II,



wherein  $M^1$  and  $M^2$  are independently P, As or Sb;  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  independently represent tertiary alkyl groups, or  $R^1$  and  $R^2$  together and/or  $R^3$  and  $R^4$  together represent an optionally substituted bivalent cycloaliphatic group whereby the two free valencies are linked to  $M^1$  or  $M^2$ , and R represents a bivalent aliphatic bridging group containing from 2 to 6 atoms in the bridge, which is substituted with two or more substituents.

2. A bidentate ligand as claimed in claim 1, wherein both  $M^1$  and  $M^2$  are phosphorus atoms.

3. A bidentate ligand as claimed in claim 1 or 2, wherein the bridging group contains from 2 to 4 carbon atoms in the bridge.

4. A bidentate ligand as claimed in any one of claims 1-3, wherein substituents are substituted at carbon-atoms of the bridging group connected with the atoms  $M^1$  and  $M^2$ .

5. A bidentate ligand as claimed in any one of claims 1-4, wherein the substituents are alkyl groups.

6. A bidentate ligand as claimed in any one of claims 1-5, wherein  $R^1$  and  $R^2$  and/or  $R^3$  and  $R^4$  together represent a bivalent substituted or non-substituted cycloalkylene group having from 6 to and including 9 ring atoms, whereby the two free valencies are linked to  $M^1$  or  $M^2$ .

7. A catalyst system including:

- (a) a source of group VIII metal cations;
- (b) a bidentate ligand as claimed in any of the claims 1-6; and
- 5 (c) a source of anions.

8. A process for the carbonylation of optionally substituted ethylenically or acetylenically unsaturated compounds by reaction with carbon monoxide and a coreactant in the presence of a catalyst system as  
10 claimed in claim 7.

9. A process as claimed in claim 8, wherein hydrogen is used as coreactant.

10. A process as claimed in claim 8, wherein a nucleophilic compound having a mobile hydrogen atom is  
15 used as coreactant.

## INTERNATIONAL SEARCH REPORT

Int Application No  
PCT/EP 01/05625

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F9/50 C07F9/6568 C07F9/6571 C07C45/50 B01J31/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CA 2 086 285 A (CYANAMID CANADA INC.) 25 June 1994 (1994-06-25) cited in the application * page 2, line 34- page 3, line 2; page 13, example 13	1-10
Y	WO 98 42717 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 1 October 1998 (1998-10-01) cited in the application the whole document	1-10
Y	WO 95 05354 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 23 February 1995 (1995-02-23) cited in the application the whole document	1-10
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

3 October 2001

Date of mailing of the international search report

12/10/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Beslier, L

## INTERNATIONAL SEARCH REPORT

In International Application No

PCT/EP 01/05625

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 495 547 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 22 July 1992 (1992-07-22) cited in the application * particularly page 6, lines 31,33,35,36,42,45 * ---	1-10
Y	US 3 527 818 A (RONALD F. MASON) 8 September 1970 (1970-09-08) the whole document -----	1-10



## INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No

PCT/EP 01/05625

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CA 2086285	A	25-06-1994	CA 2086285 A1	25-06-1994
WO 9842717	A	01-10-1998	AU 7428498 A	20-10-1998
			WO 9842717 A1	01-10-1998
			EP 0971940 A1	19-01-2000
			US 6156934 A	05-12-2000
			ZA 9802476 A	23-03-1998
WO 9505354	A	23-02-1995	AU 7614194 A	14-03-1995
			BR 9407280 A	01-10-1996
			CN 1129438 A	21-08-1996
			DE 69414578 D1	17-12-1998
			DE 69414578 T2	20-05-1999
			WO 9505354 A1	23-02-1995
			EP 0714385 A1	05-06-1996
			ES 2123823 T3	16-01-1999
			JP 9501917 T	25-02-1997
			SG 55063 A1	21-12-1998
			US 5488174 A	30-01-1996
EP 495547	A	22-07-1992	CA 2059233 A1	16-07-1992
			CA 2059236 A1	16-07-1992
			CN 1063277 A ,B	05-08-1992
			DE 69204691 D1	19-10-1995
			DE 69204691 T2	11-04-1996
			DE 69210054 D1	30-05-1996
			DE 69210054 T2	12-12-1996
			EP 0495547 A2	22-07-1992
			EP 0495548 A2	22-07-1992
			ES 2088082 T3	01-08-1996
			ES 2077337 T3	16-11-1995
			JP 5058949 A	09-03-1993
			JP 4334340 A	20-11-1992
			KR 220824 B1	15-09-1999
			SG 45352 A1	16-01-1998
			US 5210280 A	11-05-1993
US 3527818	A	08-09-1970	US 3401204 A	10-09-1968
			GB 1127965 A	25-09-1968
			BE 690123 A	24-05-1967
			DE 1593466 A1	23-07-1970
			FR 1502250 A	02-02-1968
			JP 49038278 B	16-10-1974
			NL 6616540 A ,B	29-05-1967

